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Graphene-based hybrid materials and devices for biosensing☆

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A B S T R A C T

Graphene's unique properties have made it a popular candidate for nanomaterial based biosensors. Its remarkable characteristics have led to its rapid development in the electrochemical biosensing, field effect transistors, and optical biosensing as well as the creation graphene-metal nanoparticle hybrids for improved performance. This article comprehensively reviews the most recent trends in graphene-based biosensors and attempts to identify the future directions in which the field is likely to thrive.

Contents

1. Introduction

Graphene, the thinnest material in the universe [1] is flexible, yet harder than diamond, and conducts electricity at room temperature more efficiently than any other material [2]. Graphene, which is also the basic structure of all graphitic materials, is a one-atom-thick planar sheet of sp^2 bonded carbon atoms in a honeycomb crystal lattice [3]. Its considerable attention as a next generation electronic material derives from its remarkable electronic, optical, mechanical, thermal, and electrochemical properties [4]. Molecular sensing can be achieved in this material, as graphene is electronically a very good low-noise material [4]. Substantial progress in carbon nanotube/metal nanoparticle hybrid biosensors has been achieved, however little attention has been given to the combination of graphene and nanoparticles. This review focuses on the possibilities of this synergistic combination in biosensing and some of the initial efforts in the field.

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2. Graphene properties

Graphene is often categorized by the number of stacked layers: single layer, few-layer (2–10 layers), and multi-layer which is also known as thin graphite [4]. Ideally, for graphene to preserve its distinct properties, its use should be narrowed to single or few-layer morphology. Nonetheless, advantageous properties can still be observed in thin graphite form. The number of layers needed for graphene's properties to fully match those of bulk graphite is over 100 [5]. Layer counting can be achieved by numerous methods. Among them, the most common ones are Raman spectroscopy [6], AFM [7], Rayleigh imaging [8], and optical microscopy methods [9].

The excellent electronic quality of graphene has also been a much studied subject. Its electron mobility of 15,000 $cm^2V\,s^{-1}$ at room temperature [3] and a low resistivity at low temperatures [10] rank among the best performance for any material. However, most of the remaining properties depend on the number of layers in the stack.

The electrochemical properties of graphene are also of high contemporary interest. Its main electrochemical utility is based on a wide electrochemical potential window, low charge resistance (in comparison to glassy carbon) [11], and well defined redox peaks [12]. These redox peaks are both linearly aligned with the square root of the scan rate magnitude; suggesting that redox is primarily diffusion controlled [13]. Peak-to-peak values under cyclic voltammetry are low suggesting rapid electron transfer kinetics, and its apparent electron transfer rate is orders of magnitude higher than that of glassy carbon. Graphene electrodes also exhibit high enzyme loading due to their high surface area, leading to increased sensitivity [4].

The rate of electron transfer has been shown to be surface dependent. The creation of specific surface functional groups can increase this rate significantly. The edges of graphene sheets possess a variety of oxygenated species. Work has shown that the difference in electron transfer is primarily due to the concentration of surface oxide species presented to the electrode rather than surface adsorption [14].

Recently, Luo et al. [15] studied the stability of reduced GO nanosheets in colloidal form. They found that the higher edge-to-area ratio caused by the nanoscale dimensions of the sheets changes the charge density and makes them more hydrophilic in comparison to a micro-sized GO sheet. The colloidal dispersion was stable even after centrifugation and throughout the entire range of pH values showing promise for future use as a dispersing agent for insoluble, aromatic materials.

Wang et al. [16] studied the electrochemical activity of graphene nanosheets reduced by different methods in comparison to carbon nanotubes and found that electrochemically reduced graphene and single walled nanotubes had a higher oxidation potentials (Fig. 1) and increased apparent electron transfer coefficient in comparison to chemically reduced GO nanosheets and pristine GO. They attributed the poor performance of the latter two to the presence of negatively charged moieties that weaken the electrostatic interaction between the surface and the $Fe(CN)_6{}^{4-/3-}$. Other factors that affect electron transfer kinetics are the synergetic effect of the surface chemistry, the conductivity of the materials, and the redox properties of the probe itself.

Pristine graphene has often been compared to graphene oxide. The presence of functional groups attached to the graphene sheets is the intermediary state before reduction when producing graphene from graphite oxide [11]. This form of graphene is not as electrically conductive as the pristine form and the latter has been found to have higher thermal stability. [17]

3. Synthesis of graphene

The synthesis of graphene can be categorized into three main approaches described in the following subsections.

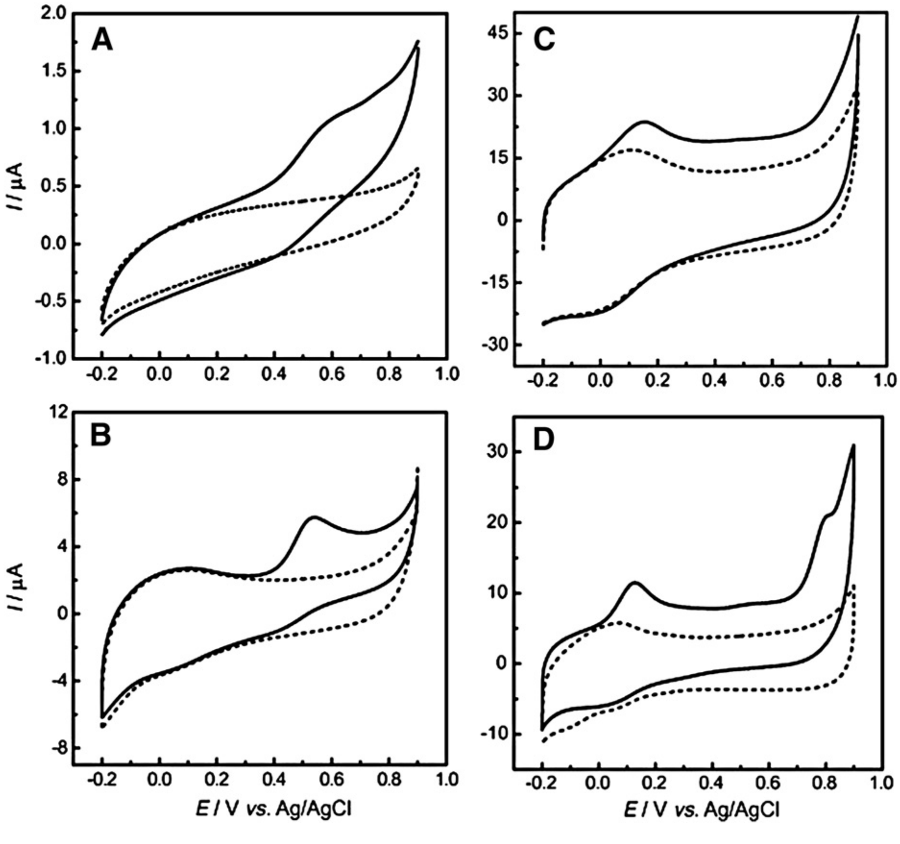

Fig. 1. CVs obtained at the pristine GONs (A), chemically reduced GONs (B), electrochemically reduced GONs (C) and SWNTs (D) in 0.10 M phosphate solution (pH 6.0) in the absence (short-dashed curves) and presence (solid curves) of 2 mM NADH. Scan rate, 20 mV s^{-1} [16].